MOISTURE-SENSITIVE CERAMICS OF THE $Li_2MoO_4 – Li_2WO_4$ SYSTEM

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New moisture-sensitive ceramic materials in the $Li_2MoO_4 – Li_2WO_4$ system were obtained. Use of these materials as humidity sensors demonstrated their promise for use in systems for controlling the moisture content of gaseous industrial media and ambient air, for example, in construction, due to the miniature nature, fast response, high sensitivity, and wide range of working temperatures and measurable relative humidity.

In addition to the traditional areas of application, ceramic materials are now being used in modern sensor technologies [1]. Technologies for production of ceramics for optical, radiation, thermal, piezoelectric, magnetic, chemisorption, temperature, and other sensors are being intensively developed. Fabricating ceramic materials for gas-sensitive elements is also of interest due to the effective combination of their process and performance characteristics: availability of fabrication, high sensitivity, fast response, reproducibility, lifetime, chemical stability, possibility of obtaining the information response in the form of an electric or optical signal, and switching with modern computer monitoring systems of different applications.

There are currently ceramic elements for gas sensors for determination of H_2, CH_4, C_3H_8, CO, H_2O, and others based on simple (NiO, WO_3, MoO_3, SnO_2, ZnO, TiO_2) and complex ($MgAl_2O_4$, $MgCr_2O_4$, Co_3O_4, $LaCaCrO_3$, $LaNiO_3$, $CaTiO_3$) oxide systems [1]. Moisture sensors occupy a special place among them due to the high degree of involvement of water vapors in different manufacturing processes. More than 100 ceramic humidity sensors that differ in composition and areas of application have been patented in Japan, the USA, Germany, and China. Most of them are oxide composites and compositions made of compounds with the structure of spinel or perovskite (Table 1).

The principle of action of ceramic humidity sensors is based on the change in the electrophysical properties of the ceramic material as a result of sorption of water molecules from the medium investigated due to dissociative chemisorption, which results in hydration of the surface of oxides, followed by physical sorption of water and formation of hydrogen bonds. Capillary condensation plays the decisive role here [8].

Ceramic humidity sensors are capable of operating in a wide range of temperatures, are miniature, and are convenient to use. However, the humidity range measured and the sensitivity of the sensor are very dependent on the microstructure of the moisture-sensitive ceramic and are determined by the accuracy of reproducing the manufacturing process for making the porous material. The mandatory presence of a heater for thermal removal of hydrate formations and vapors is a significant drawback of ceramic sensors. These heaters complicate the design, worsen the response time, and cause formation of hysteresis loops on the moisture sorption-desorption curve. These drawbacks are leading to intensive searches for new moisture-sensitive materials by foreign investigators, but there are few such developments in Russia and CIS countries.

The analysis of the structural and physicochemical properties of oxide and complex oxides showed that both lithium molybdate, Li_2MoO_4, and tungstate, Li_2WO_4, as well as compositions in the $Li_2MoO_4 – Li_2WO_4$ system, Li_2MoO_4,

TABLE 1

Chemical composition	Range of measurement of relative humidity, %	Reference
Al_2O_3, $TiO_2 – Al_2O_3$, SiO_2	20 – 95 (97)	[2, 3]
TiO_2, ZnO, $Al_2O_3 – MgO$, $Al_2O_3 – Mg – TiO_2$, $Cr_2O_3 – CaO$, $Cr_2O_3 – MgO$	0 – 100	Japanese Patent No. 4621249
$ZrO_2 – SnO_2$	30 (20) – 90	[4]
WO_3, $MnWO_3$	30 – 90	[5]
$MgFe_2O_4 – CeO_2$	4 – 90	[6]
$BaTiO_3$ doped with Ti, Zr, Hf, or Sn	20 – 80	[7]

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and Li$_2$WO (phenakite structural type, space group R3 [9]), are promising for moisture-sensitive ceramics.

Note that many modifications of water in the solid state (ice I, III) are similar to phenakite in structure, while ice II is its structural analog. Lithium molybdate does not have polymorphic transitions at atmospheric pressure, while lithium tungstate has a phenakite – spinel transition. The melting points of Li$_2$MoO$_4$ and Li$_2$WO$_4$ are 701 and 742°C, respectively. With respect to phase formation in the Li$_2$MoO$_4$ – Li$_2$WO$_4$ system, there has been no one opinion up to now — some researchers note the presence of a continuous series of solid solutions with an extremum at 720°C and a 75% molar content of lithium tungstate [10], while others talk about the existence of a limited series of solid solutions in the system with formation of a peritectic at 725°C in the 0.7 – 0.9% range of molar lithium tungstate content [11].

The results of synthesizing ceramic materials in the Li$_2$MoO$_4$ – Li$_2$WO$_4$ system and studies of their moisture-sensitive properties are reported here.

Solid-phase synthesis was conducted in a muffle furnace (in zirconium crucibles) by calcining stoichiometric mixtures of lithium carbonate Li$_2$CO$_3$, MoO$_3$, and WO$_3$ in air medium in two stages: stage I) isothermal holding of the mixture at 450°C for 2 h; stage II) isothermal holding of the composition at 620°C for 4 h. The completeness of synthesis was controlled by DTA and XPA.

DTA was performed on a MOM Paulik – Paulik – Erdey system derivatograph (Hungary) in the 293 – 1073 K temperature range at a heating and cooling rate of 10 K/min and a sample size of 0.6 – 1.0 g (standard — α-Al$_2$O$_3$). The accuracy of determining the temperature was ± 5 K.

XPA was conducted on a DRON-3M instrument (CuK$_\alpha$ radiation, Ni filter) with a plotting rate of 10 K/min.

The samples were molded on an IS-100 unit at a pressure of 100 MPa. The ceramic was made by firing molded samples in a muffle furnace: heating at the rate of 20 K/min with holding for 2 h at the sintering temperature of 873 K; cooling in the furnace cooling mode.

The temperature curves of phase resistance in the Li$_2$MoO$_4$ – Li$_2$WO$_4$ system were investigated at a frequency of 1000 Hz in a setup based on a P5030 LCR-meter on 5 × 5 × 1 mm plates (metallization of indium – gallium paste).

The moisture-sensitive properties of the ceramics materials were investigated with a Rodnik-M dynamic wet gas generator in an atmosphere of nitrogen.

Polycrystalline powders of phases of the composition Li$_2$Mo$_x$W$_{1-x}$O$_4$, where x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, were fabricated by solid-phase synthesis. The study of synthesis by the DTA method showed that phase formation in the Li$_2$MoO$_4$ – Li$_2$WO$_4$ system takes place according to a two-stage mechanism. No peaks corresponding to the phenakite – spinel polymorphic transition were found on the DTA curves for all compositions (up to Li$_2$Mo$_{0.05}$W$_{0.95}$O$_4$). The melting points of the investigated phases were accompanied by a narrow en-
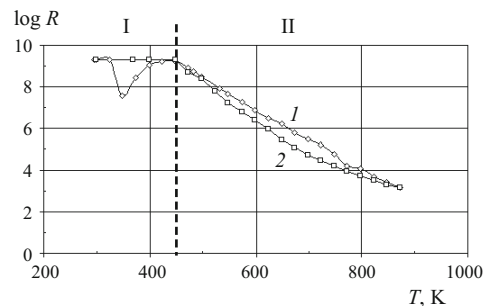


Fig. 1. Temperature curve of the resistance R of Li$_2$Mo$_{0.5}$W$_{0.5}$O$_4$ ceramic: I and II) regions of extrinsic and intrinsic conductivity; *1* and *2*) heating and cooling, respectively.

dothermic effect and increased from 974 to 1014 K with an increase in the W^{6+} content in the phase. The XPA data also confirmed the one-phase character of the synthesized polycrystalline materials of Li$_2$Mo$_x$W$_{1-x}$O$_4$ composition and their belonging to the phenakite structural type. The spinel modification was not observed. It was thus found that a continuous series of solid solutions of isovalent substitution with the structure of phenakite is formed in the Li$_2$MoO$_4$ – Li$_2$WO$_4$ system.

Ceramic materials were made from the synthesized powders to study the electrophysical and moisture-sensitive properties. The analysis of the temperature curves of the active resistance of phases in the Li$_2$MoO$_4$ – Li$_2$WO$_4$ system showed the presence of two regions of conductivity: region I ($T < 425$ K) — region of extrinsic conductivity, region II ($425 \leq T \leq 893$ K) — region of intrinsic conductivity (Fig. 1). The resistance increased in region I for all compositions of the Li$_2$MoO$_4$ – Li$_2$WO$_4$ system related to sorption of moisture on the surface and indicating the moisture-sensitive properties of these materials. In region II, the temperature curves of all compositions were monotonic in character, which indicates the absence of structural and phase changes. The temperature curves were described by the Arrhenius equation and the order of the fictitious activation energy (1.174 ± 0.397 eV). No differences were found in the shape of the temperature curves of conductivity in region II on heating and cooling, and this indicates the absence of metastable states in the structure of the solid solutions, resulting in the appearance of hysteresis.

Moisture-sensitive elements for the humidity sensors were fabricated from ceramic disk samples based on phases of Li$_2$Mo$_x$W$_{1-x}$O$_4$, where x = 0.05, 0.20, 0.30, 0.40, 0.50, and 0.70, by scribing to study the moisture-sensitive properties. Comb electrodes *2* on which current terminals *3* were soldered were applied on moisture-sensitive elements *1* by stenciling to fabricate the moisture sensors (Fig. 2). There was no heater in the sensor design.

The static and dynamic characteristics were measured for the humidity sensors. The static characteristics were the dependences of the active resistance R or capacitance C on the relative humidity φ (20 – 94% range). The static charac-
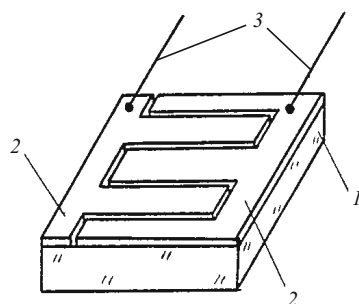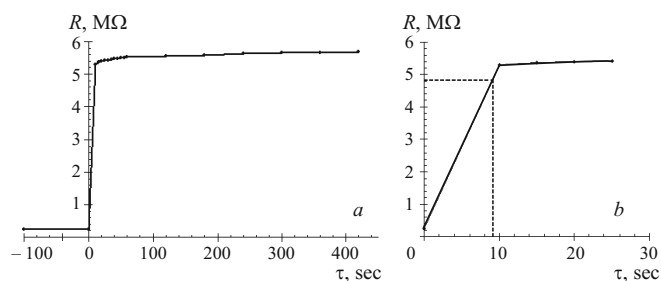
Fig. 2. Diagram of a ceramic humidity sensor.
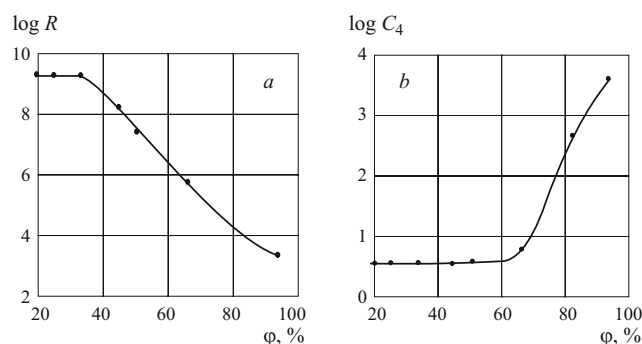
Fig. 3. Static characterization of the ceramic humidity sensor ($Li_2Mo_{0.5}W_{0.5}O_4$ composition) as a function of relative humidity φ with respect to resistance (*a*) and capacitance (*b*).

Fig. 4. Dynamic characterization with respect to resistance R of the ceramic humidity sensor ($Li_2Mo_{0.5}W_{0.5}O_4$ composition): total (*a*) and region up to 30 sec (*b*) when the relative humidity changes from 99 to 20%.

static characteristics are not a function of the method of fabrication, which indicates the predominant role of the reaction of water vapors with the structure and composition of the material.

The moisture sensitivity of the sensors is relatively high: in the 30 – 94% relative humidity range, the resistance varied from 10^9 to 10^3 Ω. The analysis of the static characteristics showed that in the concentration series, with an increase in the Li_2WO_4 content in the solid solution, the moisture sensitivity decreased. The static characteristics for the capacitance of the humidity sensors of the entire concentration series also had a monotonic character of the same shape (Fig. 3*b*). The analysis of the sensor capacitance curves as a function of the relative humidity showed that the changes in it in the 20 – 70% region are insignificant and only after 70% does the sensitivity increase sharply (change in capacitance by 3 orders of magnitude).

To determine the response time of these humidity sensors, we investigated their dynamic characteristics in sorption and desorption of water vapors, which are the change in the resistance of the sensor in time with an uneven change in the relative humidity. The study of establishment of the response of the humidity sensors showed that it can be described by the transient response of an inertial element of the first order (Fig. 4*a*) for the entire concentration series. The

teristics for the resistance of the ceramic sensors of the entire concentration series of solid solutions of $Li_2Mo_xW_{1-x}O_4$ were monotonic in nature (Fig. 3*a*) with a dynamic resistance range from 10^9 to 10^3 Ω. The moisture sensitive and electrophysical parameters of the $Li_2Mo_xW_{1-x}O_4$ ceramic materials are reported in Table 2.

We know that a difference in the porosity and microchannel size for ceramic humidity sensors unavoidably resulted in an important change in the form of the humidity characteristics due to the predominant importance of capillary condensation in formation of the information signal. We found for the moisture-sensitive ceramic investigated that the

TABLE 2

Parameter	$Li_2Mo_xW_{1-x}O_4$ composition					
	$x = 0.70$	$x = 0.50$	$x = 0.40$	$x = 0.30$	$x = 0.20$	$x = 0.05$
Working temperature range, °C	– 10 … 25	– 10 … 30	– 10 … 40	– 10 … 45	– 10 … 50	– 10 … 60
Relative humidity measurement range, %	5 – 75	5 – 80	5 – 80	5 – 80	5 – 85	5 – 95
Dynamic active resistance range, Ω:						
R_n	8.70×10^6	1.87×10^9	1.23×10^9	2.00×10^9	2.00×10^9	1.23×10^9
R_c	1.18×10^4	2.15×10^3	2.34×10^3	7.23×10^3	5.34×10^3	2.46×10^3
Sensitivity:						
with respect to resistance log R/% rel. hum.	0.248	0.138	0.124	0.115	0.104	0.090
with respect to capacitance, log C/% rel. hum.	0.275	0.122	0.205	0.097	0.122	0.114
Response time, sec	8	9	15	30	40	60

ceramic humidity sensors had a high response time (time for attaining 95% response), including in desorption — when the relative humidity changed from 99 to 20% (Fig. 4*b*). According to the existing classification of gas-analysis instruments, such sensors can be assigned to fast-response instruments (see Table 2). In comparing the response time in the concentration series, we found that the time for attaining a 95% response increased with an increase in the mole fraction of Li$_2$WO$_4$ in the solid solution.

Based on the moisture-sensitive and electrophysical properties, this ceramic is promising for creating miniature fast-response humidity sensors that operate in a wide relative humidity range, including at high temperatures, with high sensitivity.

A model of a laboratory computer system for measurement and monitoring of the moisture content of gaseous manufacturing media and ambient air during drying of brick paste was created and successfully tested based on the ceramic sensors [12].

New moisture-sensitive ceramic materials in the Li$_2$MoO$_4$ – Li$_2$WO$_4$ system were thus manufactured. The use of these materials as humidity sensors demonstrated their promise for use in systems for monitoring the moisture content of gaseous manufacturing media and ambient air, for example, in construction, due to the miniature character, fast response, high sensitivity, and wide range of working temperatures and relative humidity measured.

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